RECENT ADVANCES IN DIRECT METHANOL FUEL CELLS

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Background

The direct methanol fuel cell is based on the electro-oxidation of an aqueous solution of methanol in a polymer electrolyte membrane fuel cell without the use of a fuel processor [1]. The electro-oxidation of methanol occurs on platinum-ruthenium catalyst at the anode and the reduction of oxygen occurs on platinum catalyst at the cathode.

After the initial concept development at JPL over 6 years ago [1], there has been considerable development of the direct methanol fuel cell (DMFC) technology at the Jet Propulsion Laboratory (JPL) and at various other institutions under programs sponsored by DOD and DOE. Significant improvements in power density, efficiency, and life have been demonstrated at the cell and stack level in the last few years [1-8]. These advances in the performance of direct methanol fuel cells are sufficiently attractive for the design of complete power systems. Portable power sources, in the range of 50 - 150 W, based on this technology are currently being considered for various military applications. The development of a 150 W direct methanol fuel cell power system is currently being pursued at the Jet Propulsion Laboratory (JPL) under DARPA funding. This paper summarizes some of the recent progress in the development of cells, stacks and systems.

Cells and Stack Development

Recent cell performance obtained at JPL, employing air as the oxidant, is shown in Fig.1. These cells use Nafion 117 as the electrolyte, Pt-Ru as the anode electrocatalyst, and Pt as the cathode electrocatalyst. The platinum-ruthenium catalysts were prepared in-house. Briefly, enhancements to fuel cell performance resulted from improved techniques for fabrication of membrane-electrode assemblies, higher activity catalysts, and improved electrode structures. Platinum-ruthenium catalysts prepared in-house have so far shown significantly superior performance compared to catalyst samples obtained from commercial sources. By improving the mass transport of methanol through the anode structure, current densities as high as 800 mA/cm^2 can be achieved. Increasing the methanol concentration allows further increases in current density. As a result of these improvements, power densities as high as 230 mW/cm^2 and 300 mW/cm^2 have been demonstrated with air and oxygen, respectively.

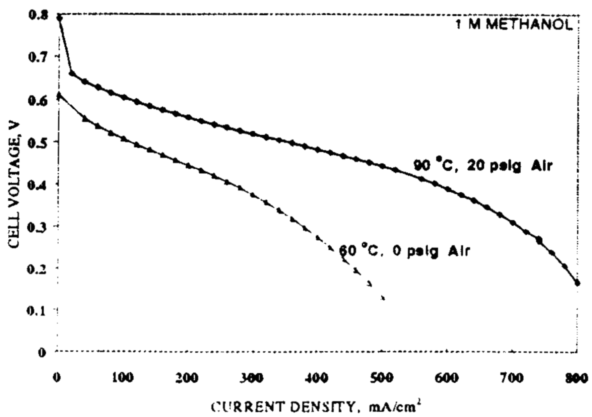

Fig. 1 Recent electrical performance of Nafion based direct methanol fuel cell.

As will be shown herein later, for portable power applications, the operation of the fuel cell stack at low stoichiometric flow rates of air is important to maintaining a thermal and water balance. The performance of the cathode at low flow rates of air is dependent significantly on the effectiveness of water removal. Improvements in the performance of the cathode have made operation at stoichiometric flow rates in the range of 1.5-2.0 possible.

It is well-known that methanol permeation through Nafion 117 impacts the efficiency of the cell significantly. Alternate membranes are being developed by the University of Southern California in collaboration with JPL that aim at reducing the crossover rates to about 10% of that of Nafion 117 without loss of electrical performance. Membranes with adequate proton conductivity and low methanol permeability can now be prepared. Fuel cells are currently being fabricated and tested using these alternate membranes. Operation at low methanol concentration of about 0.5 M also considerably reduces the crossover rates. Experiments at 60°C, have shown that operation with 0.5 M methanol results in significant gains in overall efficiency without a negative impact on power density.

Stacks based on the Nafion 117 have been fabricated in-house and in collaboration with Giner Inc. and H-Power Corporation. These stacks are aimed at operating at 60°C and low air flow rate at ambient pressure. Single cell performance has been reproduced in stacks for a wide range of operating conditions. A 5-cell stack fabricated by H-Power Corporation and 24-cell stack fabricated by Giner Inc., were tested as part of a stack development effort for a 50 W system demonstration. Improvements to stack design are now being addressed to minimize pressure drop while retaining the stack pitch of about 8 cells/inch. The overall system performance, weight and volume are governed by performance characteristics of various subsystems and their interactions with the stack. Therefore improvements at the stack level must be assessed in the system context. These are discussed in the following description of the system development efforts.

System Development

Description of direct methanol fuel cell system

A system concept based on the direct methanol fuel cell is shown in Fig. 2.

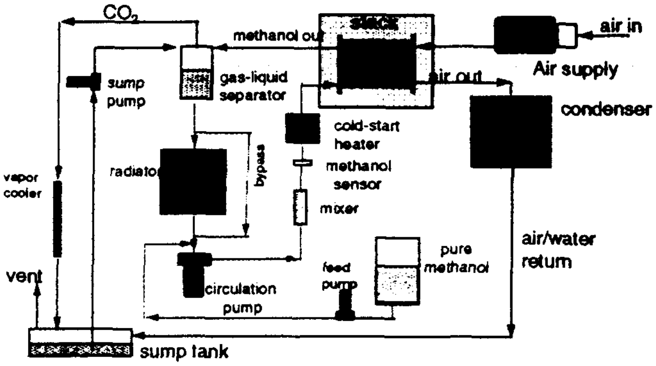

Fig. 2. Schematic of a direct methanol fuel cell system for portable applications

In this arrangement the fuel feed subsystem delivers pure methanol into a circulating loop of dilute methanol. Dilute methanol of a specified concentration constitutes the fuel solution entering the fuel cell stack. During operation, the concentration of methanol solution exiting the stack is reduced, and pure methanol must be added to restore the solution to the specified original concentration. Carbon dioxide is rejected from the solution loop at a gas-liquid separator. Air is introduced in the stack with an appropriate device such as a blower or compressor. The exiting air passes through a condenser that serves to recover water and reject heat. A portion of the recovered water may be returned to the fuel circulation loop. Additional heat rejection is accomplished by means of a heat exchanger in the fuel circulation loop. Some of the intrinsic advantages of this arrangement, relative to the hydrogen systems, are that the liquid feed of methanol allows the attainment of a uniform stack temperature and maintenance of membrane humidity.

A 50-Watt benchtop system shown in Fig. 3 was designed and operated based on the above scheme. Temperatures, methanol concentration and water produced were measured during system operation. Sustained operation for several hours demonstrated the viability of obtaining thermal and water balance in such a system.

Fig. 3. 50-Watt bench-top demonstration of methanol fuel cell system concept

System modeling studies

In the design of portable systems based on direct methanol fuel cells the most important performance parameters are: system power density (W/kg, W/L), system energy density (Wh/kg, Wh/L), efficiency (methanol to electricity), performance under transient loads, and long-term stability during operation and storage. There are several electrochemical factors that affect system performance. Among the key factors are power density as determined by the single cell characteristics, operating parameters (such as, flow rate, reactant concentration and temperature), water transport rates across the stack, and crossover rate. To understand the interaction of the stack performance and system characteristics, a closed-loop steady-state system model was developed and exercised. The model sought to relate the inputs and outputs shown in Fig. 4. The model was developed using performance data obtained on a five-cell cell stack developed at JPL. This performance data has been reported earlier [5,8]. Based on this experimental data, multi-variable mathematical correlations were developed to represent the following parametric dependencies :

a. Stack voltage on current density as a function of temperature and air flow rate.

b. Methanol Crossover rate on current density as a function of methanol concentration and temperature.

c. Water transport rates across the stack as a function of temperature and current density.

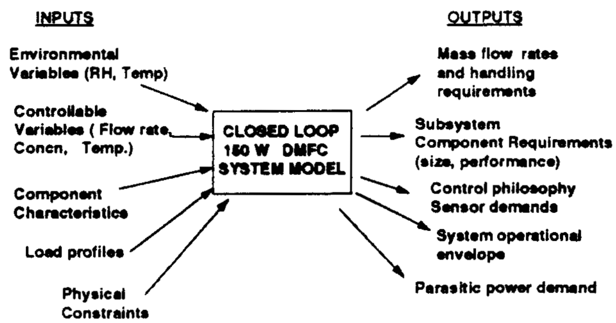

Fig. 4. Input and Outputs relating to exercising the system model

The following assumptions have been made in the model. Ambient pressure air flows across the cathodes in the stack. The air exiting the stack is saturated with water vapor. An ambient-air cooled condenser allows recovery of water and rejection of part of the heat generated in the stack. An appropriate portion of the liquid water is returned to the methanol circulation loop and the excess water is rejected. The methanol loop in the process flow diagram consists of a circulating pump, start-up heater for very low temperature start-up (<10°C), and an air-cooled radiator for heat rejection. The carbon dioxide produced in the stack is separated from the liquid stream at a gas-liquid separator. The methanol vapor carried by the exiting carbon dioxide is recovered in an air-cooled condensing unit and returned to the circulation loop.

Exercising the model shows that at stoichiometric flow rates of about 6 or greater, it is not possible to recover enough water to maintain a water balance at an ambient temperature of about 25°C. At a lower stoichiometric rate of about 3, water balance can be achieved up to an ambient temperature of 37°C. If the fuel cell system has to operate in an environmental temperature of 42°C, the stoichiometric flow rate of 3 will result in a water imbalance condition. Thus the maximum value of stoichiometric flow rate of air that will allow the maintenance of a water balance is a strong function of the ambient temperature. In order to extend the range of operation to higher ambient temperatures and also ensure water balance, we must operate at stoichiometric flow rates below 3. Therefore performance improvement at low stoichiometric flow rates is key to minimizing water loss and system weight.

By operating the stack at temperatures such as 90°C, it is possible to realize higher power densities (see Fig. 1) thus resulting in lower stack mass. However, it is now apparent from exercising the model that operation of the stack at temperatures as high as 90°C will necessarily involve intensive water recovery, and is not a desirable operating point for realizing a lightweight portable system.

The modeling results show that the efficiency of the fuel cell stacks is a strong function of the temperature and concentration. For current densities as high as 200-500 mA/cm^2, efficiencies in the range of 25-40% can be attained over a wide range of operating conditions. For lightweight portable systems, high efficiency is a prime requirement. In order to attain high efficiencies of 40% with Nafion 117 membrane, it is necessary to operate at 60°C and with 0.5 M methanol. However, the operating current density would significantly depend on the air flow rates. Experimental data at low stoichiometric flow rates[9] show that the optimal current density under these conditions is in the range 100-120 mA/cm^2.

Methanol Sensor

The modeling and experimental studies also show that at 60°C the efficiency decreases with increasing methanol. Thus, operating a fuel cell to maintain the maximum efficiency needs close control of methanol concentration and temperature. Maintenance of concentration of methanol requires an in-line concentration sensor that has a response time sufficient to react to the control requirements in a system. Therefore, at JPL we have developed a fast and robust sensor for monitoring methanol concentration. This has been successfully implemented in the methanol circulation loop (see Figs. 2 and 3). With this sensor the concentration can be controlled and the system output can be maintained at a steady value. Such a sensor was found to perform satisfactorily in a 50 Watt system concept demonstration. This sensor design will be adopted for the 150 Watt packaged power source currently under development.

Acknowledgment

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